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Published in:
Applied Physics Letters

DOI:
[10.1063/1.3656713](https://doi.org/10.1063/1.3656713)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2011

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Kuik, M., Vandenberg, J., Goris, L., Begemann, E. J., Lutsen, L., Vanderzande, D. J. M., Manca, J. V., & Blom, P. W. M. (2011). Optical detection of deep electron traps in poly(p-phenylene vinylene) light-emitting diodes. *Applied Physics Letters*, 99(18), 183305-1-183305-3. [183305]. <https://doi.org/10.1063/1.3656713>

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Optical detection of deep electron traps in poly(*p*-phenylene vinylene) light-emitting diodes

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(Received 26 July 2011; accepted 9 October 2011; published online 1 November 2011)

The trap-limited electron currents in poly(*p*-phenylene vinylene) (PPV) derivatives can be modeled using a Gaussian trap distribution that is positioned approximately 0.75 eV below the lowest unoccupied molecular orbital (LUMO) of PPV. Photothermal deflection spectroscopy measurements and internal photo-emission spectroscopy measurements confirm the claim of a Gaussian shaped trap distribution centered at 0.75 eV below the LUMO of PPV. Additionally, two PPV derivatives that differ in the number of conformational defects incorporated during synthesis exhibit identical electron trapping behavior, showing that the traps do not originate from extrinsic impurities of the synthesis or defects in the polymer chains. © 2011 American Institute of Physics. [doi:10.1063/1.3656713]

In order to increase the efficiency of polymer light-emitting diodes (PLEDs), a fundamental understanding of the charge transport is vital. Investigation of the charge transport in PLEDs of poly(*p*-phenylene vinylene) (PPV) derivatives has led to the insight that charge transport is dominated by space-charge-limited hole current¹ whereas the electron transport is trap limited.^{2,3} As a consequence, the electrons drift less far into the PLED as compared to the holes. A major disadvantage of the presence of electron traps in the carrier transport is that the recombination process as well as the recombination zone is consequently heavily perturbed. It has recently been shown that non-radiative recombination via trap states is the dominant recombination mechanism in PLEDs at low voltages.^{4,5} Furthermore, due to the reduced electron transport, a large amount of excitons is formed close to the cathode, resulting in an energy transfer to the metallic cathode followed by non-radiative decay.⁶ Both effects lead to a loss of light-output efficiency, especially at low voltages.⁴⁻⁶ Therefore, knowledge about the presence and position of trap levels in PLED materials is of vital importance for optimizing the luminous efficiency.

The exact origin of the traps giving rise to the trap-limited electron current in semiconducting polymers is still under debate. Defects such as kinks in the polymer backbone,^{7,8} impurities remaining from the synthesis, or contamination from the environment⁹ have been proposed as possible sources. Techniques such as thermally stimulated currents (TSC) and deep level transient spectroscopy (DLTS) have been employed to obtain information on the properties of traps.¹⁰⁻¹² From a transport perspective, by elimination of trapping by n-type doping, it has convincingly been shown that the traps that govern the electron current in PPV are located at least 0.4 eV below the lowest unoccupied molecular orbital (LUMO) and are thus well separated from the Gaussianly distributed (LUMO) density of states (DOS).¹³

In the last decade, the trap-limited electron current (TLC) in organic semiconductors has been generally described as free electron transport in the LUMO in the presence of an exponential distribution of electron traps inside the band gap.² This exponential distribution of traps leads to a strong voltage and layer-thickness dependence of the current-voltage (*J-V*) characteristics, as derived by Mark and Helfrich.² However, a drawback of this model is that the actual trap depth as well as the total amount of traps cannot be determined independently. Recently, it has been demonstrated by Nicolai *et al.* that the TLC in PPVs can be equally well described when a, more intuitive, Gaussian trap distribution is assumed.¹⁴ In this work, it is suggested that various PPVs share a common trap origin and a trap depth of about 0.7–0.8 eV below the LUMO is deduced.

In this letter, we apply two optical techniques to visualize the electron trap distributions directly. Photothermal deflection spectroscopy (PDS) measurements clearly reveal the presence of a trap distribution 0.75 eV below the LUMO of PPV. Additionally, we present internal photo-emission spectroscopy (IPE) measurements that again convey a trap level at about 0.75 eV below the LUMO of the polymer. Finally, we compare the trapping behavior of two types of poly[2-methoxy-5-(3', 7'-dimethyloctyloxy)-*p*-phenylene vinylene] (MDMO-PPV) that only differ in their synthesis, leading to different amounts of conformational defects. However, electrical modeling of their electron transport and PDS measurements reveals an identical Gaussian trap distribution 0.75 eV below the LUMO. This shows that conformational defects induced in the synthesis are not responsible for the electron trapping in MDMO-PPV.

MDMO-PPV is a very common material in organic electronics. Both in the field of light-emitting diodes (LEDs) and solar cells this compound has served as a workhorse during the last decades. A common synthetic approach used to obtain MDMO-PPV is a dehydrohalogenation route, also called “Gilch” route, which uses a dichloro-substituted

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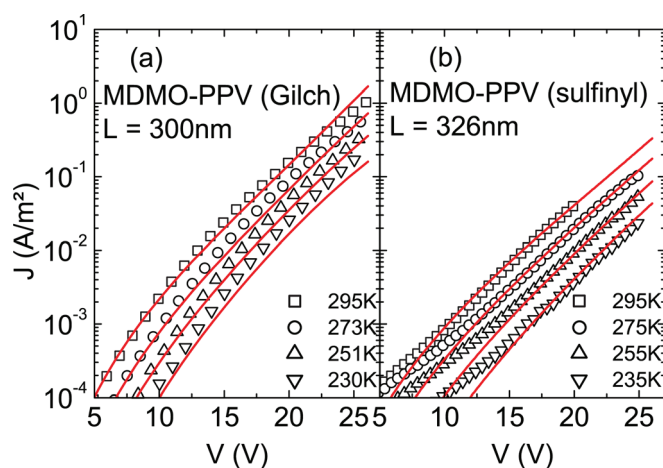


FIG. 1. (Color online) Experimental (open symbols) and calculated (solid lines) J - V characteristics of a (a) 300 nm MDMO-PPV (Gilch) and a (b) 326 nm MDMO-PPV (sulfinyl) electron-only device at different temperatures.

monomer.^{15,16} An alternative synthesis procedure is the “sulfinyl” route, which utilizes an asymmetric chloro-, sulfinyl-substituted monomer.^{17,18} The asymmetry in the sulfinyl monomer leads to a higher regularity in the polymer due to less head-to-head or tail-to-tail additions during polymerization. Consequently, “sulfinyl” MDMO-PPV constitutes fewer defects that may act as trap sites than regular “Gilch” MDMO-PPV.

To investigate their electron transport, electron-only devices were fabricated; consisting of the structure glass/Al/MDMO-PPV/Ba/Al.^{19,20} These crossbar structured devices were fabricated in a cleanroom environment and kept in nitrogen from the moment the bottom contact of 30 nm Al was thermally deposited in vacuum. The polymer layer was consequently spin-coated from toluene after which the structure was topped with a thermally evaporated 5 nm Ba and 100 nm Al, again in vacuum. The current density measurements (J - V) were performed in a nitrogen atmosphere as well. Figure 1(a) depicts the trap-limited electron current at different temperatures for a 300 nm “Gilch” MDMO-PPV layer. Since typically trap-limited transport exhibits hysteresis all the temperature scans have been performed on fresh devices.²¹ For the analysis of the trap depth, a benchmarked numerical device model²² is used that incorporates drift and diffusion of charge carriers, the effect of space charge on the electric field and a density-dependent mobility.²³ The trapping description used in this model is characterized by a Gaussian trap distribution as implemented by Nicolai *et al.*¹⁴ and Paasch *et al.*²⁴ Identical to an earlier report, the parameters for the Gaussian trap distribution amount to $N_t = 1.3 \times 10^{23} \text{ m}^{-3}$, $\sigma_t = 0.1 \text{ eV}$ and a trap depth of 0.71 eV below the LUMO.¹⁴ For comparison, Fig. 1(b) illustrates the J - V characteristics of a 326 nm “sulfinyl” MDMO-PPV layer. Modeling in this case leads to equal parameters as for the “Gilch” variant being, $N_t = 1.3 \times 10^{23} \text{ m}^{-3}$, $\sigma_t = 0.1 \text{ eV}$, where only the trap level is lowered slightly to 0.74 eV in order to obtain a better fit. The higher regularity in the polymer chain of “sulfinyl” MDMO-PPV leads to less processability of the solution.¹⁷ Therefore the deviation of the fit at lower voltages is caused by parasitical currents in the device and not by the bulk properties of the transport layer. Summa-

rizing, modeling on the electron current demonstrates that the trapping behavior for both materials is exactly the same.

Having established again that the trap depth needed to describe the TLC in PPVs is about 0.75 eV below the center of the (LUMO) DOS, we would like to confirm this value via direct measurements. A very sensitive technique for measuring non-radiative decay in thin films is PDS. In this technique the absorption of light of a certain sub-gap wavelength can invoke local non-radiative decay that produces local heating. When the sample is immersed in a liquid characterized by small changes in temperature and large changes in refractive index the probe beam parallel to the surface of the sample (HeNe laser) is able to detect very subtle changes in $\alpha(E)$, the optical absorption coefficient. The samples were prepared by drop casting the MDMO-PPV solution onto Corning 7056 quartz substrates ($6 \times 12 \text{ mm}$) in nitrogen atmosphere. A detailed description for this method is described elsewhere.²⁵ All spectra are set on an absolute absorption coefficient scale by measuring separately the transmission/reflection of the PDS-films. Figure 2 shows the PDS results for both materials. Below 1.1 eV, multiphonon absorptions are visible due to vibrational overtones of C-H stretching and bending vibrations.^{26,27} At 1.35 eV, a clear broad peak is discernible after which an incline, due to transitions originating from the tail of the DOS, is observed. It should be noted that optical excitation is a relative measurement, since it also involves the exciton binding energy. An electron is excited from the highest occupied molecular orbital (HOMO) into a higher energy state. In our measurements, the HOMO-LUMO transition clearly starts to show up for excitation energies that exceed 2 eV. To correct for exciton binding energy effects, the position of the broad peak at 1.35 eV inside the band-gap should be taken relative to the onset of the HOMO-LUMO absorption peak, located at $\sim 2.1 \text{ eV}$. As a result, the sub-band-gap absorption at 1.35 eV corresponds with the presence of a Gaussian trap at about 0.75 eV below the LUMO. Also apparent from Fig. 2 is that the position of the trap for both “Gilch” and “sulfinyl” MDMO-PPV is at exactly the same energy level, which in turn agrees with the modeling of the J - V characteristics.

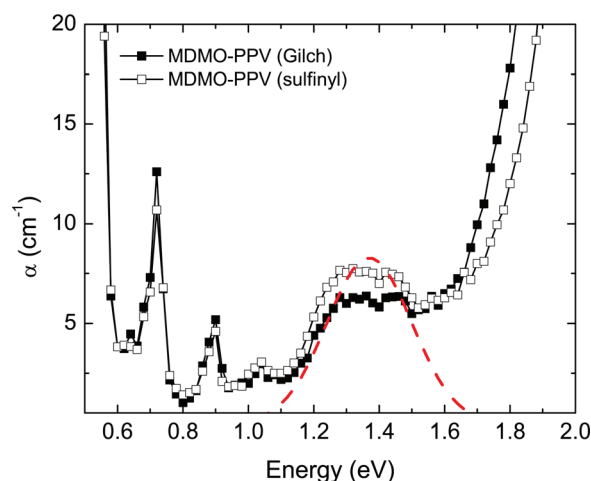


FIG. 2. (Color online) PDS spectra of “Gilch” and “sulfinyl” MDMO-PPV. The dashed curve serves as a guide to the eye for the position of the Gaussian trap distribution at about 0.75 eV below the LUMO for both synthesis routes.

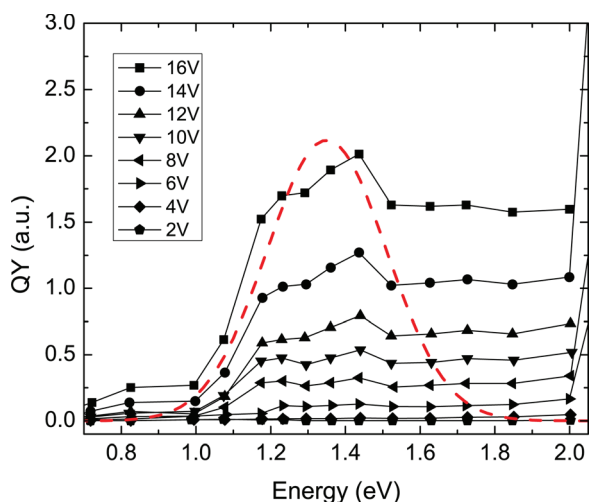


FIG. 3. (Color online) IPE spectra for a 700 nm “Gilch” MDMO-PPV device at different driving voltages. The dashed curve serves as a guide to the eye for the position of the Gaussian trap distribution, again at about 0.75 eV below the LUMO.

As an alternative to the PDS measurements, another type of optical probe technique is presented. IPE is a common and useful tool to investigate energy level differences, e.g., barrier heights at a metal/semiconductor interface.²⁸ In general this technique comprises the probing of an induced photocurrent caused by the excitation of charge carriers. Samples were prepared analogue to the fabrication of the electron-only devices, only in this case pre-patterned glass/ITO substrates were used and the devices were topped with thermally evaporated Ca and Al. Figure 3 depicts the IPE measurement on the resulting glass/ITO/“Gilch” MDMO-PPV/Ca/Al structure comprising a 700 nm polymer layer where the device is irradiated from the ITO side. Since ITO and Ca are known to form ohmic contacts with MDMO-PPV, we can exclude any contribution to the IPE measurements from contact barriers, only transitions inside the band gap of the material will be probed. The samples were irradiated by a Xenon lamp through a series of filters in order to obtain monochromatic light. Since the photocurrent can be very small a lock-in amplifier is used to detect the resulting signal at a chop frequency of 40 Hz. A discernible signal onset is centered around 1.35 eV in Fig. 3. This peak is exactly at the same position as the peak in the PDS measurements. In the IPE measurement, this again corresponds to the fact that electrons from the HOMO are excited into an empty trap level that is located about 0.75 eV below the onset of the HOMO-LUMO absorption. In doing so, the electron transport driven by the applied electric field is improved since the fermi level in the device increases due to additional filling up of empty traps. Furthermore, at higher voltages, the chance for electrons to escape from a trap and contribute to a photocurrent increases due to local barrier lowering and tunneling. Above 1.6 eV the signal stays relatively high due to excitation from the HOMO into the tail of the LUMO DOS. To summarize, also this measurement technique demonstrates the position of the onset to agree well with the calculations of a Gaussian trap at about 0.75 eV below the LUMO.

In conclusion, we have verified the presence of deep electron traps in MDMO-PPV by two different types of opti-

cal measurements. Both PDS and IPE confirm the trap position of 0.75 eV below the LUMO that was derived from electrical modeling of the electron transport. Furthermore, we have compared the trap-limited electron current of common “Gilch” MDMO-PPV to that of “sulfinyl” MDMO-PPV. Although the “sulfinyl” variant constitutes a higher regularity in the polymer chain, and therefore possibly less trap sites, no difference in trapping behavior was observed. These results strongly suggest that PPVs share a common physical origin for the trap-limited electron current.

The authors would like to acknowledge the technical assistance of J. Harkema and F. van der Horst and the financial support of the Fund for Scientific Research-Flanders (FWO) (Ph.D. Grant for J.V.). We also want to thank the Institute for the Promotion of Innovation by Science and Technology in Flanders (IWT) for the financial support via the IWT-SBO project 060843 “Polyspec.”

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